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(54) Hair cleansing composition

(57) Provided is a hair cleansing composition containing (A) an amphipathic amide lipid, (B) an anionic surfactant and (C) an organic or inorganic acid, or a salt thereof, and having a pH of from 1 to 4.5 when diluted with water to 20 times the weight.

The hair cleansing composition of the present invention has advantages including protecting hair from physical or chemical stimulation and preventing split

ends or breakage of hair without impairing the cleansing ability and feeling upon use, imparting hair with a pleasant feeling to the touch and moisture retention properties such as natural smoothness, moist feeling, and suppleness which healthy hair inherently possesses, and has excellent stability.

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Description**FIELD OF THE INVENTION**

5 [0001] The present invention relates to acid hair cleansing compositions containing an amphipathic amide lipid.

BACKGROUND OF THE INVENTION

10 [0002] Since hair is daily exposed to physical stimulation by daily hair care routines such as heat drying with a hair dryer and brushing, and chemical stimulation by shampooing, permanent waving, dyeing and bleaching, it is in a damaged state with a partial loss of components or structure. A change in hair quality due to ageing accelerates this damage and also causes the loss of suppleness which healthy hair inherently possesses.

15 [0003] It is a common practice to protect or repair hair in a damaged state by making up for the lost components or structure or an analogue thereof. Interaction (affinity) between a protecting base and hair is considered to be important for developing a protecting or restoring function, and thus a method of using a sphingolipid or protein derivative as a protecting base has been employed widely as a useful technique. For example, proposed is a hair cleansing composition containing a surfactant composed of an anionic surfactant and a bipolar ionic surfactant, a cationic polymer, and ceramide or glyccoceramide (Japanese Patent Application Laid-Open No. 59443/1996). The composition however cannot contain a sufficient amount of a protecting base such as a ceramide or glyccoceramide because it has a high melting point and is liable to crystallize. Moreover, even a slight amount of the protecting base incorporated in the composition does not readily penetrate into hair. No method has yet been proposed to feed hair with a sufficient amount of a protecting base. The conventional hair cleansing compositions are therefore accompanied by the problem that the protecting base incorporated therein cannot fully function.

SUMMARY OF THE INVENTION

25 [0004] According to the present invention, there is thus provided a hair cleansing composition containing the following components (A) to (C):

- 30 (A): an amphipathic amide lipid,
 (B): an anionic surfactant, and
 (C): an organic or inorganic acid, or a salt thereof, and having a pH of from 1 to 4.5 at 25°C when diluted with water to 20 times the weight.

DETAILED DESCRIPTION OF THE INVENTION

[0005] The present invention relates to a hair cleansing composition which allows a protecting base to sufficiently penetrate into hair and has excellent effects for preventing or repairing damaged hair.

40 [0006] The present inventors have found that acidification of the composition facilitates penetration of the amphipathic amide lipid serving as a protecting base into hair even in a cleansing composition system, thereby making it possible to protect hair from physical or chemical stimulation, suppress generation of split ends or breakage of hair, and at the same time impart hair with a pleasant feeling to the touch such as natural smoothness, moist feeling, and suppleness which healthy hair inherently possesses.

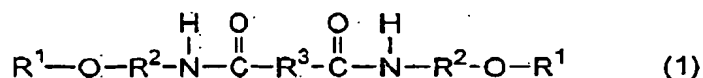
45 [0007] The amphipathic amide lipid as Component (A) preferably has 1 or 2 amide groups; preferably has, as a carbon chain bonded to the carbonyl group of the amide group, a C₅₋₆₀ alkyl or alkylene group which may be substituted with a hydroxy group and may contain an ester bond in its main chain; and preferably contains 1 to 5 hydroxy or C₁₋₃₀ alkoxy groups in total. The following compounds (1) to (4) are specific preferred examples of the amphipathic amide lipid.

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(1) Diamide compounds represented by formula (1):

[0008]



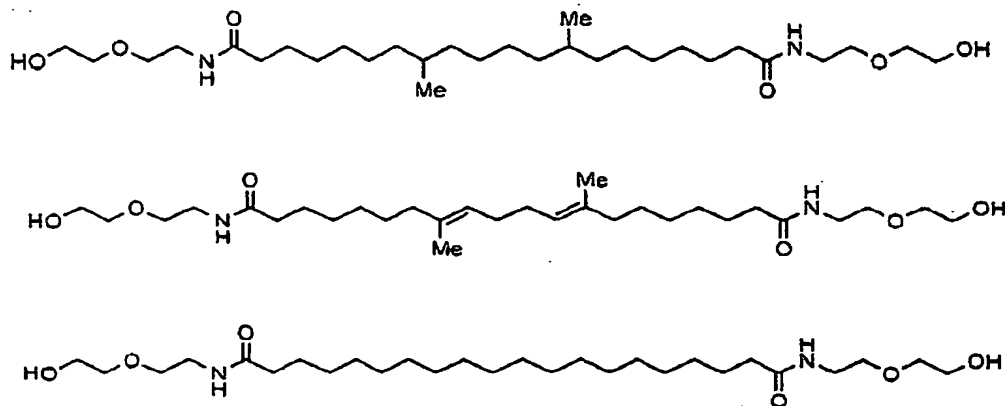
wherein, R¹ represents a linear or branched C₁₋₁₂ hydrocarbon group which may be substituted with a hydroxy group (s) and/or alkoxy group(s), R² represents a linear or branched divalent C₁₋₅ hydrocarbon group and R³ represents a linear or branched divalent C₁₋₂₂ hydrocarbon group.

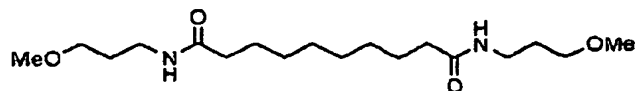
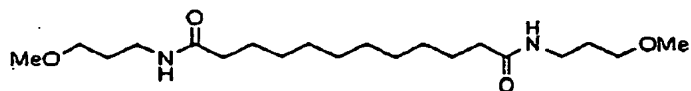
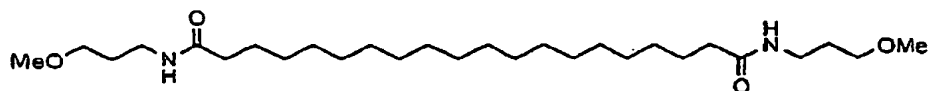
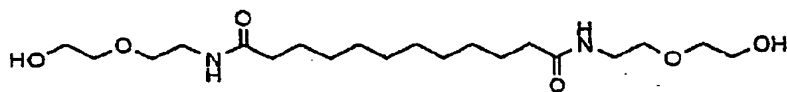
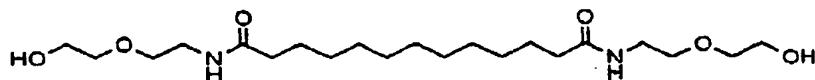
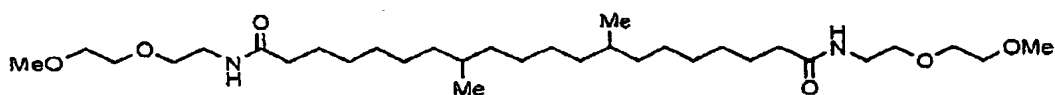
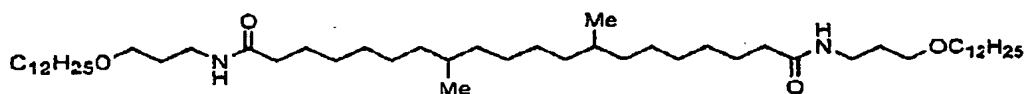
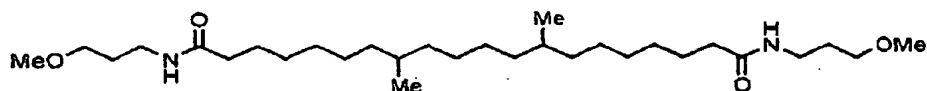
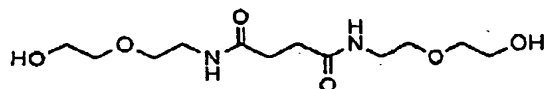
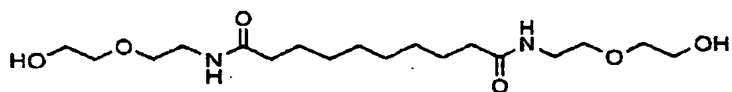
[0009] As R¹ in formula (1), linear or branched C₁₋₁₂ alkyl groups which may be substituted with 1 to 3 groups selected from the group consisting of a hydroxy group and C₁₋₆ alkoxy groups are preferred. Of these, unsubstituted C₁₋₁₂ alkyl groups and C₂₋₁₂ alkyl groups substituted with 1 to 2 hydroxy groups and one C₁₋₆ alkoxy group or with one hydroxy group and one C₁₋₆ alkoxy group are more preferred. Specific examples include methyl, ethyl, propyl, butyl, hexyl, dodecyl, 2-methylpropyl, 2-ethylhexyl, 2-hydroxyethyl, 9-hydroxynonyl, 2,3-dihydroxypropyl, 2-methoxyethyl, 2-hydroxy-3-methoxypropyl and 9-methoxynonyl groups, of which 2-hydroxyethyl, methyl, dodecyl and 2-methoxyethyl groups are preferred.

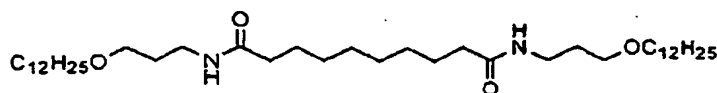
[0010] As R² in formula (1), linear or branched C₂₋₅ alkylene groups are preferred, and linear or branched C₂₋₃ alkylene groups are preferred. Specific examples include ethylene, trimethylene, tetramethylene, pentamethylene, 1-methylcyclohexene, 2-methylcyclohexene, 1-methyltrimethylene, 2-methyltrimethylene, 1,1-dimethylethylene and 2-ethyltrimethylene groups. Of these, ethylene and trimethylene groups are preferred.

[0011] As R³ in formula (1), linear or branched divalent C₂₋₂₂ hydrocarbon groups are preferred, and linear or branched C₁₁₋₂₂ alkylene groups and alkenylene groups having 1 to 4 double bonds are more preferred. Specific examples include ethylene, trimethylene, tetramethylene, hexamethylene, heptamethylene, octamethylene, decamethylene, undecamethylene, dodecamethylene, tridecamethylene, tetradecamethylene, hexadecamethylene, octadecamethylene, 1-methylethylene, 2-ethyltrimethylene, 1-methylheptamethylene, 2-methylheptamethylene, 1-butylhexamethylene, 2-methyl-5-ethylheptamethylene, 2,3,6-trimethylheptamethylene, 6-ethyldecamethylene, 7-methyltetradecamethylene, 7-ethylhexadecamethylene, 7,12-dimethyloctadecamethylene, 8,11-dimethyloctadecamethylene, 7,10-dimethyl-7-ethylhexadecamethylene, 1-octadecylethylene, ethenylene, 1-octadecenylethylene, 7,11-octadecadienylene, 7-ethenyl-9-hexadecamethylene, 7,12-dimethyl-7,11-octadecadienylene and 8,11-dimethyl-7,11-octadecadienylene groups. Of these, 7,12-dimethyloctadecamethylene, 7,12-dimethyl-7,11-octadecadienylene, octadecamethylene, undecamethylene and tridecamethylene groups are preferred.

[0012] Preferred diamide compounds (1) are compounds having the above-described preferred groups as R¹, R² and R³, respectively. Specific examples are the following compounds:

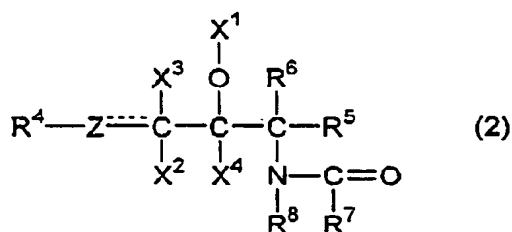






(2) Ceramides represented by the following formula (2):

[0013]



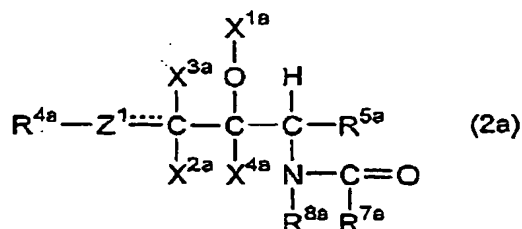
wherein, R⁴ represents a linear, branched or cyclic, saturated or unsaturated C₄₋₃₀ hydrocarbon group which may be substituted with hydroxy, oxo or amino group(s), Z represents a methylene group, a methine group or an oxygen atom, a broken line represents the presence or absence of a π bond, X¹ represents a hydrogen atom, an acetyl group or a glyceryl group, or, together with the adjacent oxygen atom, forms an oxo group, X², X³ and X⁴ each independently represents a hydrogen atom, a hydroxy group or an acetoxy group (with the proviso that when Z represents a methine group, one of X² and X³ represents a hydrogen atom and the other does not exist, and when -O-X¹ represents an oxo group, X⁴ does not exist), R⁵ and R⁶ each independently represents a hydrogen atom, a hydroxy group, a hydroxymethyl group or an acetoxymethyl group, R⁷ represents a linear, branched or cyclic, saturated C₅₋₃₅ hydrocarbon group which may be substituted with a hydroxy or amino group, or the saturated C₅₋₃₅ hydrocarbon group in which a linear, branched or cyclic, saturated or unsaturated C₈₋₂₂ fatty acid which may be substituted with hydroxy group(s) is ester-bonded at the ω-position of the hydrocarbon group, and R⁸ represents a hydrogen atom or a linear or branched, saturated or unsaturated hydrocarbon group which may have substituent(s) selected from a hydroxy group, hydroxyalkoxy groups, alkoxy groups and an acetoxy group, and has 1 to 8 carbon atoms in total.

[0014] As R⁴ in formula (2), linear, branched or cyclic, saturated or unsaturated C₇₋₂₂ hydrocarbon groups which may be substituted with hydroxy group(s) are preferred. As X¹, a hydrogen atom and a glyceryl group are preferred. It is preferred that none or one of X², X³, and X⁴ represents a hydroxy group and the others represent a hydrogen atom. It is preferred that one of R⁵ and R⁶ represents a hydrogen atom or a hydroxymethyl group and the other represents a hydrogen atom. In R⁷, preferred examples of the fatty acid which may be ester-bonded or amide-bonded to the saturated hydrocarbon group at the ω-position thereof include isostearic acid, 12-hydroxystearic acid and linoleic acid. As R⁸, a hydrogen atom and hydrocarbon groups which may be substituted with 1 to 3 substituents selected from a hydroxy group, hydroxyalkoxy groups and alkoxy groups and have 1 to 8 carbon atoms in total are preferred.

[0015] As ceramide (2), preferred are the following compounds (2a) and (2b).

(2a) Natural ceramides or natural type ceramides represented by formula (2a), and derivatives thereof (which will hereinafter be called "natural type ceramides")

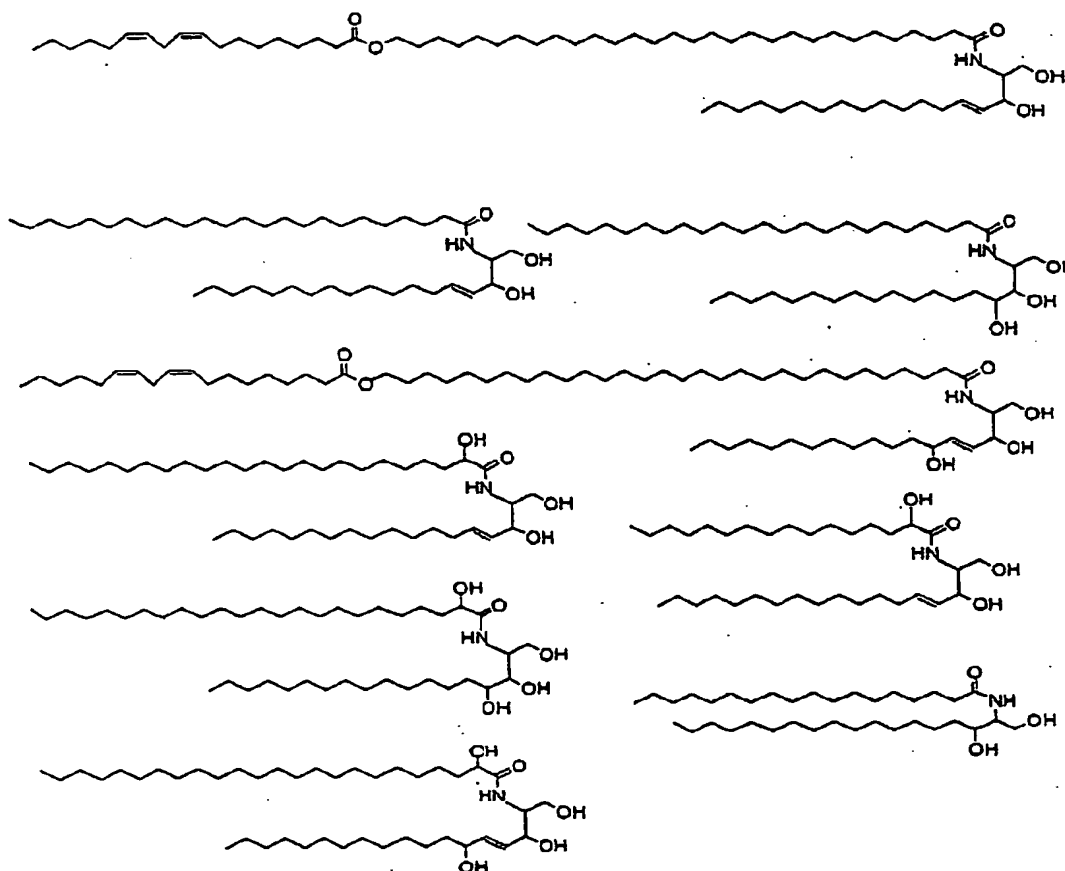
[0016]



wherein, R^{4a} represents a linear, branched or cyclic, saturated or unsaturated C₇₋₁₉ hydrocarbon group which may be substituted with a hydroxy group, Z¹ represents a methylene or methine group, a broken line represents the presence or absence of a π bond, X^{1a} represents a hydrogen atom or, together with the adjacent oxygen atom, forms an oxo group, X^{2a}, X^{3a} and X^{4a} each independently represents a hydrogen atom, a hydroxy group or an acetoxy group (with the proviso that when Z¹ represents a methine group, one of X^{2a} and X^{3a} represents a hydrogen atom and the other does not exist, and when -O-X^{1a} represents an oxo group, X^{4a} does not exist), R^{5a} represents a hydroxymethyl group or an acetoxymethyl group, R^{7a} represents a linear, branched or cyclic, saturated C₅₋₃₀ hydrocarbon group which may be substituted with hydroxy group(s), or the saturated C₅₋₃₀ hydrocarbon group in which a linear or branched, saturated or unsaturated C₈₋₂₂ fatty acid which may be substituted with hydroxy group(s) is ester-bonded at the ω -position of the hydrocarbon group, and R^{8a} represents a hydrogen atom or a C₁₋₄ alkyl group.

[0017] Preferred are compounds in which R^{4a} is a linear C₇₋₁₉, more preferably C₁₃₋₁₅ alkyl group, Z¹ is a methine group, one of X^{2a} and X^{3a} is a hydrogen atom, and R^{7a} is a linear C₉₋₂₇ alkyl group which may be substituted with hydroxy group(s). In addition, X^{1a} preferably represents a hydrogen atom or, together with an oxygen atom, forms an oxo group. More preferred examples of R^{7a} include a tricosyl group, a 1-hydroxypentadecyl group, a 1-hydroxytricosyl group, a heptadecyl group, a 1-hydroxyundecyl group and a nonacosyl group having a linoleic acid ester-bonded at the ω -position of the group.

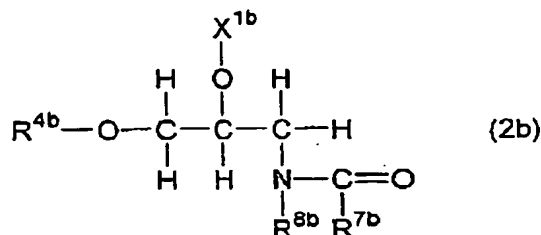
[0018] Specific examples of the natural type ceramides include Ceramide Types 1 to 7 having the below-described structures and obtained by amidation of sphingosine, dihydrosphingosine, phytosphingosine or sphingadienine (for example, FIG. 2 of J. Lipid Res., 24, 759(1983), and pig and human ceramides as described in FIG. 4 of J. Lipid Res., 35, 2069(1994)).



[0019] Examples also include N-alkyl derivatives (for example, N-methyl derivatives) of the above-described ceramides. They may be either a natural extract or synthesized product. Commercially available ones are also usable.

(2b) Pseudo type ceramides represented by the following formula (2b):

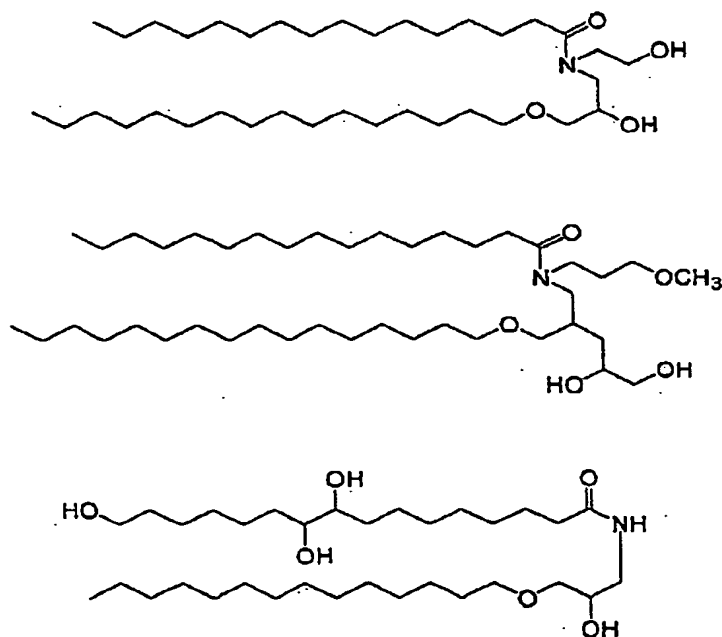
[0020]



wherein, R^{4b} represents a linear, branched or cyclic, saturated or unsaturated C_{10-22} hydrocarbon group which may be substituted with hydroxy group(s), X^{1b} represents a hydrogen atom, an acetyl group or a glyceryl group, R^{7b} represents a linear, branched or cyclic, saturated or unsaturated C_{5-22} hydrocarbon group which may be substituted with hydroxy or amino group(s), or the hydrocarbon group in which a linear or branched, saturated or unsaturated C_{8-22} fatty acid which may be substituted with hydroxy group(s) is ester-bonded at the ω -position of the hydrocarbon group, and R^{8b} represents a hydrogen atom or an alkyl group which may be substituted with hydroxy group(s), hydroxyalkoxy group(s), alkoxy group(s) or acetoxy group(s) and has 1 to 8 carbon atoms in total.

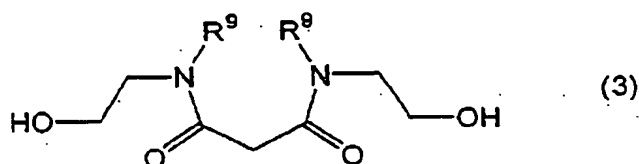
[0021] Preferred as R^{7b} are a nonyl group, a tridecyl group, a pentadecyl group, an undecyl group having linoleic acid ester-bonded at the ω -position of the group, a pentadecyl group having linoleic acid ester-bonded at the ω -position of the group, a pentadecyl group having 12-hydroxystearic acid ester-bonded at the ω -position of the group, and an undecyl group having methyl-branched isostearic acid amide-bonded at the ω -position of the group. As the hydroxyalkoxy or alkoxy groups for R^{8b} , preferred are those having 1 to 8 carbon atoms.

[0022] As the pseudo type ceramides (2b), those having as R^{4b} a hexadecyl group, as X^{1b} a hydrogen atom, as R^{7b} a pentadecyl group, and as R^{8b} a hydroxyethyl group; those having as R^{4b} a hexadecyl group, as X^{1b} a hydrogen atom, as R^{7b} a nonyl group, and as R^{8b} a hydroxyethyl group; or those having as R^{4b} a hexadecyl group, as X^{1b} a glyceryl group, as R^{7b} a tridecyl group, and as R^{8b} a 3-methoxypropyl group are preferred, with those having as R^{4b} a hexadecyl group, as X^{1b} a hydrogen atom, as R^{7b} a pentadecyl group, and as R^{8b} a hydroxyethyl group being more preferred. Specific preferred examples include those represented by the following formulas:



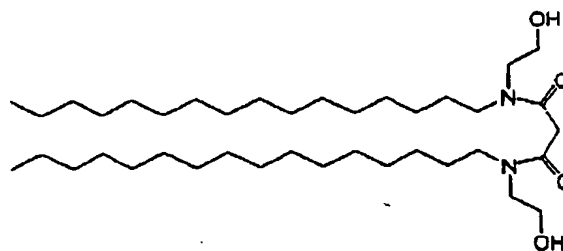
(3) Diamide compounds represented by the following formula (3) :

[0023]



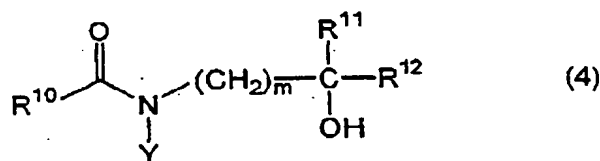
wherein, R^9 represents a C_{10-18} alkyl group which may be substituted with hydroxy group(s).

[0024] Specific examples of compound (3) include the compound represented by the following formula:

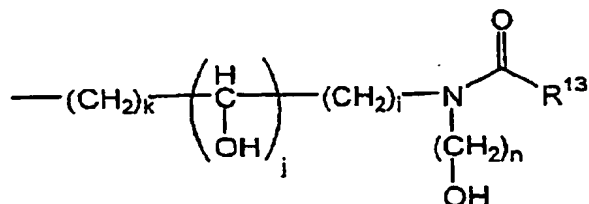


(4) Amide compounds represented by the following formula (4) :

[0025]

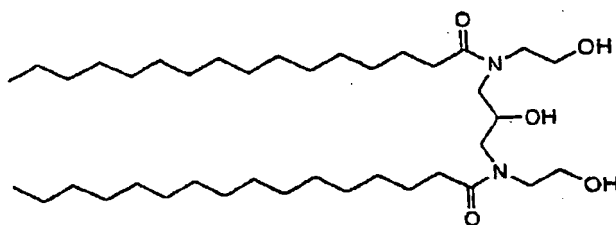


wherein, R^{10} represents a linear or branched, saturated or unsaturated C_{9-31} alkyl group which may be substituted with hydroxy group(s), or a 2-dodecen-1-yl succinic acid residue, m stands for an integer of from 1 to 3, R^{11} and R^{12} each represents a hydrogen atom or a C_{1-4} alkyl or hydroxyalkyl group, Y represents a linear or branched, saturated or unsaturated C_{10-32} alkyl group which may be substituted with hydroxy group(s), or a substituent represented by the following formula:



in which, k , i and n each stands for an integer of from 1 to 3, j stands for 0 or 1, and R^{13} represents a linear or branched, saturated or unsaturated C_{9-31} alkyl group which may be substituted with hydroxy group(s).

[0026] Specific examples of Compound (4) include a compound represented by the following formula:



[0027] Of the above-described amphipathic amide lipids, those represented by formula (1) or (2) are preferred, and those represented by formula (1) are more preferred.

[0028] As Component (A), two or more of these amphipathic amide lipids may be used in combination. Its (their) content in the hair cleansing composition of the present invention is preferably by weight of the composition, from 0.001 to 20 wt.%, more preferably from 0.1 to 15 wt.%, even more preferably from 0.2 to 3 wt.% in view of imparting suppleness to hair and preventing split ends or breakage of hair.

[0029] The anionic surfactants as Component (B) include alkyl (or alkenyl) sulfates, polyoxyalkylene alkyl (or alkenyl) ether sulfates, alkane sulfonates, olefin sulfonates, alkylbenzene sulfonates, alkyl (or alkenyl) sulfosuccinates, dialkyl (or dialkenyl) sulfosuccinates, polyoxyalkylene alkyl (or alkenyl) sulfosuccinates, alkyl (or alkenyl) ether carboxylates, polyoxyalkylene alkyl (or alkenyl) ether carboxylates, polyoxyalkylene alkyl (or alkenyl) ether phosphates, fatty acid salts, N-acyl glutamates, N-acyl taurates, and N-acylmethyltaurine. Of these, polyoxyethylene alkyl ether sulfates, polyoxyethylene alkenyl ether sulfates and alkyl sulfates are preferred, with those represented by the below-described formula (B1) or (B2) being more preferred.



wherein, R^{14} represents a C_{10-18} alkyl or alkenyl group, R^{15} represents a C_{10-18} alkyl group, M represents an alkali metal, alkaline earth metal, ammonium, alkanolamine or basic amino acid, and a is a weight average number of from 1 to 5.

[0030] As Component (B), two or more of the above-described compounds may be used in combination. Its (their) content in the hair cleansing composition of the present invention is preferably by weight of the composition, from 1 to 50 wt.%, more preferably from 8 to 30 wt.%, even more preferably from 10 to 22 wt.% from the viewpoint of foaming properties, liquid properties during use and cleansing ability.

[0031] Examples of the organic acid as Component (C) include carboxylic acids such as monocarboxylic acids, dicarboxylic acids, hydroxycarboxylic acids and polycarboxylic acids, alkylsulfuric acids and alkylphosphoric acids. Of these, carboxylic acids are preferred and dicarboxylic acids and hydroxycarboxylic acids are more preferred. The dicarboxylic acids include malonic acid, succinic acid, glutaric acid, adipic acid, maleic acid, fumaric acid, phthalic acid and glutamic acid, of which glutamic acid is preferred. The hydroxycarboxylic acids include glycolic acid, lactic acid, hydroxyacrylic acid, oxybutyric acid, glyceric acid, malic acid, tartaric acid and citric acid, of which α -hydroxycarboxylic acids are preferred and lactic acid, malic acid and glycolic acid are more preferred. Examples of the inorganic acid include phosphoric acid, sulfuric acid and nitric acid, with phosphoric acid being preferred.

[0032] As Component (C), two or more of the above-described organic or inorganic acids, or salts thereof may be used in combination. Its (their) content in the hair cleansing composition of the present invention is, in terms of an acid, preferably by weight of the composition, from 0.05 to 10 wt.%, more preferably from 0.1 to 5 wt.% even more preferably from 0.5 to 2 wt.% in view of promoting the penetration of Component (A) (amphipathic amide lipid) into hair.

[0033] For improving foaming performance, a surfactant other than Component (B), preferably a nonionic surfactant or amphoteric surfactant may be incorporated in the hair cleansing composition of the present invention.

[0034] Examples of the nonionic surfactant include polyoxyalkylene sorbitan fatty acid esters, polyoxyalkylene sorbitol fatty acid esters, polyoxyalkylene glycerin fatty acid esters, polyoxyalkylene fatty acid esters, polyoxyalkylene alkyl ether fatty acid esters, polyoxyalkylene alkylphenyl ethers, polyoxyalkylene (hydrogenated) castor oils, sucrose fatty acid esters, polyglycerin alkyl ethers, polyglycerin fatty acid esters, fatty acid alkanolamides, alkyl glycosides and glyceryl ethers. Of these, alkyl glycosides, polyoxyalkylene (C_8 to C_{20}) fatty acid esters, polyoxyethylene sorbitan fatty acid esters, polyoxyethylene hydrogenated castor oils and fatty acid alkanolamides are preferred. As the fatty acid alkanolamides,

those having a C₈₋₁₈ acyl group are preferred and those having a C₁₀₋₁₆ acyl group are more preferred. As the fatty acid alkanolamides, either monoalkanolamides or dialkanolamides may be used, with those having a C₂₋₃ hydroxyalkyl group being preferred. Examples thereof include oleic diethanolamide, palm kernel fatty acid diethanolamide, coconut oil fatty acid diethanolamide, lauric acid diethanolamide, polyoxyethylene coconut oil fatty acid monoethanolamide, oil fatty acid diethanolamide, lauric acid isopropanolamide and lauric acid monoethanolamide.

oil fatty acid diethanolamide, lauric acid isopropanolamide and lauric acid monoethanolamide.

[0035] As the amphoteric surfactant, betaine surfactants are preferred, with fatty acid amidopropyl imethylaminoacetic acid betaines and fatty acid amidopropyl betaines, those having a C₈₋₁₈ acyl group are preferred betaines being more preferred. As the fatty acid amidopropyl betaines, those having a C₈₋₁₈ acyl group are more preferred, with laurylamidopropyl betaine, palm kemelamidopropyl betaine

and cocamidopropyl betaine being even more preferred. Its (or their) content in the whole composition

[0036] Two or more of these surfactants may be used in combination. Its (or their) content in the whole composition is preferably from 0.01 to 20 wt.%, more preferably from 0.05 to 10 wt.%, even more preferably from 0.1 to 5 wt.%. In the composition of the present invention, silicone derivatives or cationic polymers ordinarily

[0037] To the hair cleansing composition of the present invention, silicone derivatives can be added further for improving the feeling upon use. The silicone derivatives include dimethylpolysiloxane, methylphenylpoly-

[0038] Examples of the silicone derivatives include dimethylpolysiloxane, methylphenylpolysiloxane, amino-modified silicones, polyether-modified silicones, epoxy-modified silicones, fluorine-modified silicones, cyclic silicones, alkyl-modified silicones and oxazoline-modified silicones, of which dimethylpolysiloxane, methylphenylpolysiloxane, amino-modified silicones, polyether-modified silicones, oxazoline-modified silicones and cyclic silicones are preferred. Two or more of these silicones may be used in combination. Its (or their) content in the whole composition is preferably from 0.05 to 10 wt.%, even more preferably from 0.1 to 5 wt.%. It is most

from 0.01 to 20 wt.%, more preferably from 0.05 to 10 wt.%, even more preferably from 0.1 to 5 wt.%.

[0039] Examples of the cationic polymer include polydimethyldiallylammonium chlorides, acrylamide/polydimethylammonium chloride/acrylate copolymers, acrylamide/dimethyldiallylammonium chloride copolymers, methylvinylimmonium chloride/acrylate copolymers, acrylamide/dimethyldiallylammonium chloride copolymers, methylvinylimmonium chloride/vinylpyrrolidone copolymers, hydroxyethyl cellulose/diallyldimethylammonium chloride copolymers, diethylsulfates of vinylpyrrolidone/dimethylaminoethyl methacrylate copolymers, vinylpyrrolidone/dimethylaminoethyl methacrylate copolymers, vinylpyrrolidone/alkylaminoacrylate/vinylcaprolactam copolymers, vinylpyrrolidone/dimethylaminopropylmethacrylamide copolymers, chlorinated O-[2-hydroxy-3-(trimethylammonio)propyl]hydroxy cellulose, and guar hydroxypropyltrimonium chloride. Of these, chlorinated O-[2-hydroxy-3-(trimethylammonio)propyl]hydroxy cellulose and guar hydroxypropyltrimonium chloride are preferred from the viewpoint of the feeling. Two or more of these may be used in combination. Its (or their) content in the whole composition is, as a solid content, from 0.1 to 5 wt. %.

of these cationic polymers may be used in combination. Its (or their) content in the whole composition, preferably from 0.1 to 5 wt.%, content, preferably from 0.01 to 20 wt.%, more preferably from 0.05 to 10 wt.%, even more preferably from 0.1 to 5 wt.%, of the composition of the present invention can contain, in addition to the above-described com-

[0040] The hair cleansing composition of the present invention can contain, in addition to the above-described components, oil components such as higher alcohols, lanolin derivatives, and polyethylene glycol fatty acid esters; water soluble polymers such as hydroxypropylmethyl cellulose, hydroxy cellulose, polyvinyl alcohol, and polyethylene glycol; polyhydric alcohols such as sorbitol; humectants; chelating agents such as ethylenediaminetetraacetic acid (EDTA); drugs such as vitamin preparations; amino acids and derivatives thereof; fine particles of a polymer such as polyethylene, polystyrene, poly(methyl methacrylate), nylon or silicone, and hydrophobic products thereof; extracts derived from animals or plants; ultraviolet absorbers; pearling agents; antiseptics; bactericides; pH regulators; colorants; and fragrances, according to the intended use.

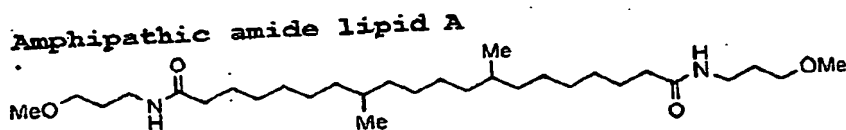
[0041] The hair cleansing composition of the present invention is adjusted to have a pH of from 1 to 4.5 upon application to hair (diluted with water to 20 times the weight of the composition; at 25°C). This allows for example, Component (A) (amphipathic amide lipid) to sufficiently penetrate into hair and prevents irritation. The pH of the composition is preferably from 2 to 4, more preferably from 3 to 4.

(A) (amphipathic amide lipid) to 500 mg, preferably from 2 to 4, more preferably from 3 to 4.

[0042] The hair cleansing composition of the present invention can be provided in any form such as liquid, powder, gel or granule as needed. A liquid composition using water or a lower alcohol as a solvent is preferred, with an aqueous solution being more preferred.

-Examples-

[0043] The following examples further describe and demonstrate embodiments of the present invention. The examples are given solely for the purpose of illustration and are not to be construed as limitations of the present invention. In the below-described Examples and Comparative Examples, the following amphipathic amide lipids were employed.



(2) The physical property-recovering ratio of hair

[0047] About 20 g (about 15 to 20 cm in length) of the hair of a Japanese female, which had not been subjected to any chemical treatment such as permanent waving and hair dyeing, was treated eight times with "LAVENUS High Bleach" (trade name; product of Kao Corporation) (bath ratio 1:1), each at 40°C for 20 minutes. After each bleaching treatment, cleansing with a plain shampoo and a plain rinse was conducted 90 times, 720 times in total. The plain shampoo and plain rinse used here have the following compositions, respectively:

· Plain Shampoo

[0048]

	(wt.%)
A 25 wt.% solution of sodium polyoxyethylene	62.0
(2.5) lauryl ether sulfate	2.28
Lauric acid diethanolamide	0.10
Disodium edetate	0.50
Sodium benzoate	0.03
Oxybenzone	0.10
Phosphoric acid (75 wt.%)	0.01
Dibutylhydroxytoluene	0.80
Sodium chloride	0.00012
Red No. 106	0.26
Fragrance	Balance
Purified water	

· Plain Rinse

[0049]

	(wt.%)
Stearyltrimethylammonium chloride (28 wt.%)	2.7
Distearyldimethylammonium chloride	3.6
Cetanol	2.0
Propylene glycol	5.0
Methyl p-hydroxybenzoate	0.1
Deionized water	Balance

[0050] Dynamic viscoelasticity (storage elastic modulus E' : corresponding to the hardness of hair, unit: [Pa]) of each of a hair bundle (healthy hair) without treatment, a hair bundle subjected to the above-described bleaching treatment and a hair bundle shampooed with the shampoo of Table 1 30 times after the bleaching treatment was measured using a dynamic viscoelasticity-measuring apparatus "DMTA V" (trade name; product of Rheometric Scientific FE).

· Measuring conditions

[0051] Temperature: $22 \pm 1^\circ\text{C}$, relative humidity: $20 \pm 1\%$ RH, frequency: 10 Hz

· Criteria for evaluation

[0052] A physical property-recovering ratio of hair R represented by the following equation:

$$R = (E_1' - E_n') / (E_1' - E_0') \times 100$$

wherein, E_0' represents a storage elastic modulus of the healthy hair, E_1' represents a storage elastic modulus of the bleached hair and E_n' represents a storage elastic modulus of the hair shampooed 30 times with each sample after bleaching, was calculated as an index of how the physical properties of hair damaged by the bleaching treatment were recovered by the treatment with each sample of Table 1 compared with those of hair before bleaching (untreated hair), and each sample was evaluated based on the below-described criteria:

- A: not less than 70 and up to 100
 B: not less than 50 but less than 70
 C: less than 50

Table 1

		(wt.%)					
		Examples			Comparative Examples		
		1	2	3	1	2	3
(A)	Amphipathic amide lipid A	2	2	-	2	-	-
	Amphipathic amide lipid B	-	-	2	-	-	-
(B)	Sodium polyoxyethylene (2) lauryl ether sulfate	10	10	10	10	10	10
	Sodium lauryl sulfate	5	5	5	5	5	5
(C)	Lactic acid	1	-	1	1	1	-
	Malic acid	-	1	-	-	-	-
Others	Myristyl alcohol	1	1	1	1	1	1
	Cocoylmonoethanolamide	0.5	0.5	0.5	0.5	0.5	0.5
	Ethylene glycol distearate	1	1	1	1	1	1
	Cationized hydroxyethyl cellulose	0.3	0.3	0.3	0.3	0.3	0.3
	Cationized guar gum	0.5	0.5	0.5	0.5	0.5	0.5
	PH regulator (sodium hydroxide, citric acid)	q.s.*	q.s.*	q.s.*	q.s.*	q.s.*	q.s.*
	Purified water	Balance	Balance	Balance	Balance	Balance	Balance
pH		3.5	3.5	3.5	5	3.5	6
Evaluation	Smoothness of hair	A	A	A	C	C	C
	Moist feeling of hair	A	A	A	C	C	C
	Physical property-recovering ratio of hair	A	A	B	C	C	C

*An amount to adjust the pH

Example 4: Clear shampoo

[0053]

	(wt.%)
Sodium polyoxyethylene (2) lauryl ether sulfate	10.0
Sodium lauryl sulfate	5.0
Cationized guar gum	0.1
Amphipathic amide lipid A	0.2

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(continued)

	(wt.%)
Malic acid	0.75
Sodium chloride	1.0
Laurylamidopropyl betaine	1.0
Cocoylmonoethanolamide	0.3
Propylene carbonate	0.5
Glycerin	1.0
Sodium hydroxide	An amount to adjust the pH balance
Deionized water	

[0054] The above-described shampoo (pH 4.0) can provide hair with good smoothness, moist feeling and suppleness after use.

Example 5 Conditioning shampoo

[0055]

	(wt.%)
Sodium polyoxyethylene (2) lauryl ether sulfate	8.0
Sodium lauryl sulfate	5.0
Cationized guar gum	0.5
Amphipathic amide lipid A	2.0
Maleic acid	0.75
Trisodium citrate	1.0
Laurylamidopropyl betaine	3.0
2-Ethylhexyl monoglyceryl ether	0.7
Myristyl alcohol	1.0
Ethylene glycol distearate	3.0
Polypropylene glycol (Mw=400)	0.5
Glycerin	1.0
Sodium hydroxide	An amount to adjust the pH balance
Deionized water	

[0056] The above-described shampoo (pH 3.5) can provide hair with good smoothness, moist feeling and suppleness after use.

Example 6: Conditioning shampoo

[0057]

	(wt.%)
Sodium polyoxyethylene (2) lauryl ether sulfate	11.0
Sodium lauryl sulfate	5.0
Cationized guar gum	0.3
Amphipathic amide lipid B	2.0
Malic acid	0.75
Lactic acid	0.1
Sodium chloride	0.2
Benzyl alcohol	0.5
Cocoylmonoethanolamide	1.0
Myristyl alcohol	1.0

(continued)

	(wt.%)
Cetanol	0.5
Ethylene glycol distearate	3.0
Cationic hydroxyethyl cellulose	0.3
Glycerin	1.0
Sodium hydroxide	An amount to adjust the pH balance
Deionized water	

[0058] The above-described shampoo (pH 3.7) can provide hair with good smoothness, moist feeling and suppleness after use.

Example 7: Conditioning shampoo

[0059]

	(wt.%)
Sodium polyoxyethylene (2) lauryl ether sulfate	8.0
Cationized guar gum	0.3
Amphipathic amide lipid C	0.05
Amphipathic amide lipid D	0.1
Malic acid	0.5
Lactic acid	0.5
Sodium chloride	1.0
Laurylamidopropyl betaine	3.0
Myristyl alcohol	1.0
Cetanol	0.5
Behentrimonium chloride	0.5
Ethylene glycol distearate	2.0
Benzoyloxyethanol	0.5
Sodium hydroxide	An amount to adjust the pH balance
Deionized water	

[0060] The above-described shampoo (pH 3.9) can provide hair with good smoothness, moist feeling and suppleness after use.

Example 8: Conditioning shampoo

[0061]

	(wt.%)
Sodium polyoxyethylene (2) lauryl ether sulfate	8.0
Sodium lauryl sulfate	5.0
Cationized guar gum	0.5
Amphipathic amide lipid E	2.0
Glycolic acid	1.0
Trisodium citrate	1.0
Laurylamidopropyl betaine	3.0
2-Ethylhexyl monoglyceryl ether	0.7
Myristyl alcohol	1.0
Ethylene glycol distearate	3.0
Propylene glycol (Mw=400)	0.5

(continued)

	(wt.%)
Glycerin	1.0
Sodium hydroxide	An amount to adjust the pH
Deionized water	balance

[0062] The above-described shampoo (pH 3.5) can provide hair with good smoothness, moist feeling and suppleness after use.

Example 9: Conditioning shampoo

[0063]

	(wt.%)
Sodium polyoxyethylene (2) lauryl ether sulfate	8.0
Cationized guar gum	0.3
Amphipathic amide lipid C	0.05
Amphipathic amide lipid D	0.1
Malic acid	0.5
Glutamic acid	1.0
Sodium chloride	1.0
Laurylamidopropyl betaine	3.0
Myristyl alcohol	1.0
Cetanol	0.5
Behenyltrimonium chloride	0.5
Ethylene glycol distearate	2.0
Benzyloxyethanol	0.5
Sodium hydroxide	An amount to adjust the pH
Deionized water	balance

[0064] The above-described shampoo (pH 3.9) can provide hair with good smoothness, moist feeling and suppleness after use.

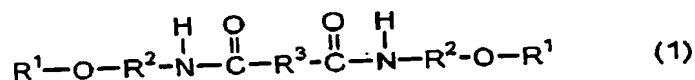
Claims

1. A hair cleansing composition comprising the following components (A) to (C):

- (A): an amphipathic amide lipid,
- (B): an anionic surfactant, and
- (C): an organic or inorganic acid, or a salt thereof,

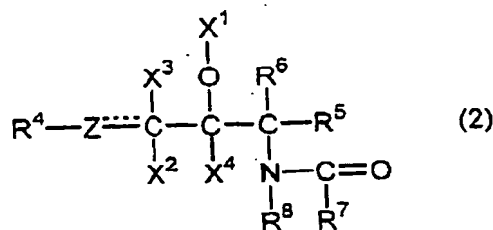
wherein the composition has a pH of from 1 to 4.5 at 25°C when diluted with water to 20 times the weight of the composition.

2. The hair cleansing composition of Claim 1, wherein Component (A) is an amphipathic amide lipid selected from the group consisting of compounds represented by the following formulas (1) to (4) and mixtures thereof:

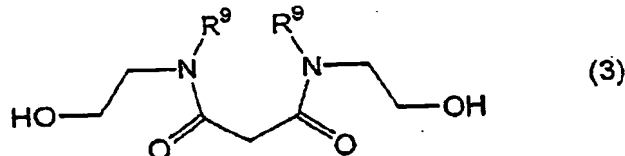


wherein, R¹ represents a linear or branched C₁₋₁₂ hydrocarbon group which may be substituted with a hydroxy

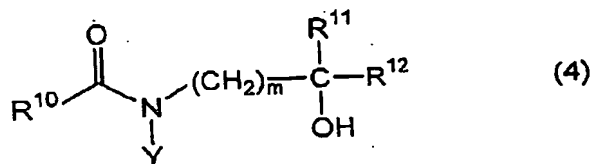
group(s) and/or alkoxy group(s), R² represents a linear or branched divalent C₁₋₅ hydrocarbon group and R³ represents a linear or branched divalent C₁₋₂₂ hydrocarbon group,



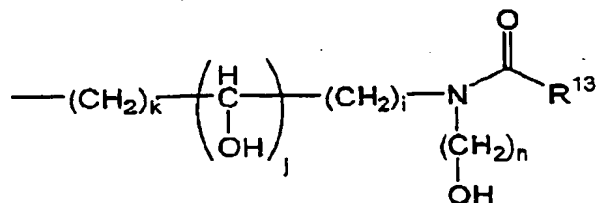
wherein, R⁴ represents a linear, branched or cyclic, saturated or unsaturated C₄₋₃₀ hydrocarbon group which may be substituted with hydroxy, oxo or amino group(s), Z represents a methylene group, a methine group or an oxygen atom, a broken line represents the presence or absence of a π bond, X¹ represents a hydrogen atom, an acetyl group or a glyceryl group, or, together with the adjacent oxygen atom, forms an oxo group, X², X³ and X⁴ each independently represents a hydrogen atom, a hydroxy group or an acetoxymethyl group (with the proviso that when Z represents a methine group, one of X² and X³ represents a hydrogen atom and the other does not exist, and when -O-X¹ represents an oxo group, X⁴ does not exist), R⁵ and R⁶ each independently represents a hydrogen atom, a hydroxy group, a hydroxymethyl group or an acetoxymethyl group, R⁷ represents a linear, branched or cyclic, saturated C₅₋₃₅ hydrocarbon group which may be substituted with a hydroxy or amino group(s), or the saturated C₅₋₃₅ hydrocarbon group in which a linear, branched or cyclic, saturated or unsaturated C₈₋₂₂ fatty acid which may be substituted with hydroxy group(s) is ester-bonded at the ω -position of the hydrocarbon group, and R⁸ represents a hydrogen atom or a linear or branched, saturated or unsaturated hydrocarbon group which may have substituent(s) selected from a hydroxy group, hydroxyalkoxy groups, alkoxy groups and an acetoxymethyl group, and has 1 to 8 carbon atoms in total



wherein, R⁹ represents a C₁₀₋₁₈ alkyl group which may be substituted with hydroxy group(s).

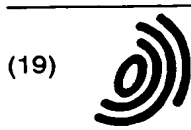


wherein, R¹⁰ represents a linear or branched, saturated or unsaturated C₉₋₃₁ alkyl group which may be substituted with hydroxy group(s), or a 2-dodecen-1-yl succinic acid residue, m stands for an integer of from 1 to 3, R¹¹ and R¹² each represents a hydrogen atom or a C₁₋₄ alkyl or hydroxyalkyl group, Y represents a linear or branched, saturated or unsaturated C₁₀₋₃₂ alkyl group which may be substituted with hydroxy group(s), or a substituent represented by the following formula:



in which, k, i and n each stands for an integer of from 1 to 3, j stands for 0 or 1, and R¹³ represents a linear or branched, saturated or unsaturated C₉₋₃₁ alkyl group which may be substituted with hydroxy group(s).

3. The hair cleansing composition of Claim 1, wherein Component (B) is an anionic surfactant selected from the group consisting of alkyl (or alkenyl) sulfates, polyoxyalkylene alkyl (or alkenyl) ether sulfates, alkane sulfonates, olefin sulfonates, alkylbenzene sulfonates, alkyl (or alkenyl) sulfosuccinates, dialkyl (or dialkenyl) sulfosuccinates, polyoxyalkylene alkyl (or alkenyl) sulfosuccinates, alkyl (or alkenyl) ether carboxylates, polyoxyalkylene alkyl (or alkenyl) ether carboxylates, polyoxyalkylene alkyl (or alkenyl) ether phosphates, fatty acid salts, N-acyl glutamates, N-acyl taurates, and N-acylmethyltaurine, and mixtures thereof.
4. The hair cleansing composition of Claim 1, wherein Component (C) is an organic or inorganic acid, or a salt thereof selected from the group consisting of monocarboxylic acids, dicarboxylic acids, hydroxycarboxylic acids and polycarboxylic acids, alkylsulfuric acids and alkylphosphoric acids, and mixtures thereof.
5. The hair cleansing composition of Claim 1, further comprising a component selected from the group consisting of silicone derivatives, cationic polymers, and mixtures thereof.
6. The hair cleansing composition of Claim 1, wherein the pH of the composition is from 2 to 4.
7. The hair cleansing composition of Claim 1, further comprising a surfactant selected from the group consisting of nonionic surfactant, amphoteric surfactant, and mixtures thereof.
8. The hair cleansing composition of Claim 1, comprising from 0.001 to 20 wt. % of Component (A).
9. The hair cleansing composition of Claim 1, comprising from 1 to 50 wt. % of Component (B).



(19)

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(54) Hair cleansing composition

(57) Provided is a hair cleansing composition containing (A) an amphipathic amide lipid, (B) an anionic surfactant and (C) an organic or inorganic acid, or a salt thereof, and having a pH of from 1 to 4.5 when diluted with water to 20 times the weight.

The hair cleansing composition of the present invention has advantages including protecting hair from physical or chemical stimulation and preventing split

ends or breakage of hair without impairing the cleansing ability and feeling upon use, imparting hair with a pleasant feeling to the touch and moisture retention properties such as natural smoothness, moist feeling, and suppleness which healthy hair inherently possesses, and has excellent stability.

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EUROPEAN SEARCH REPORT

Application Number
EP 03 02 9670

DOCUMENTS CONSIDERED TO BE RELEVANT					
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (In I.C.I.7)		
X	EP 0 739 625 A (OREAL) 30 October 1996 (1996-10-30) * page 12, lines 5-10; claims; examples * * page 9, line 57 - page 11, line 17 * * page 11, lines 28,29 *	1-3,5-9	A61K7/06		
X	US 5 661 118 A (DUBIEF CLAUDE ET AL) 26 August 1997 (1997-08-26) * column 14, lines 21-26; claims; examples * * column 10, line 25 - column 12, line 58 * column 13, lines 8,9 *	1-3,5-9			
X	EP 1 166 766 A (KAO CORP) 2 January 2002 (2002-01-02) * paragraphs [0013], [0023], [0024], [0046]; example 3 *	1-9			
A	K. DE POLO: "A short Textbook of Cosmetology" 1998, VERLAG FÜR CHEMISCHE INDUSTRIE, AUGSBURG, GERMANY, XP002295514 * pages 65-69 *	1-9	<table border="1"> <thead> <tr> <th>TECHNICAL FIELDS SEARCHED (In I.C.I.7)</th> </tr> </thead> <tbody> <tr> <td>A61K</td> </tr> </tbody> </table>	TECHNICAL FIELDS SEARCHED (In I.C.I.7)	A61K
TECHNICAL FIELDS SEARCHED (In I.C.I.7)					
A61K					
<p>The present search report has been drawn up for all claims</p>					
Place of search Berlin		Date of completion of the search 10 September 2004	Examiner Boeker, R		
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p>		<p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons 8 : member of the same patent family, corresponding document</p>			

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Application Number:

EP 03 02 9670

CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing more than ten claims.

- ☐ Only part of the claims have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims and for those claims for which claims fees have been paid, namely claim(s):
- ☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims.

LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

see sheet B

- ☐ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.
- ☐ As all searchable claims could be searched without effort justifying an additional fee, the Search Division did not invite payment of any additional fee.
- ☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:
- ☒ None of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims:

1-9 (in part)



European Patent
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**LACK OF UNITY OF INVENTION
SHEET B**

Application Number
EP 03 02 9670

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

1. claims: 1-9 (in part)

Hair cleansing compositions comprising a compound of formula
(1), an anionic surfactant, a silicone and an acid

2. claims: 1-9 (in part)

Hair cleansing compositions comprising a compound of formula
(2), an anionic surfactant, a silicone and an acid

3. claims: 1-9 (in part)

Hair cleansing compositions comprising a compound of formula
(3), an anionic surfactant, a silicone and an acid

4. claims: 1-9 (in part)

Hair cleansing compositions comprising a compound of formula
(4), an anionic surfactant, a silicone and an acid

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 03 02 9670

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
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10-09-2004

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0739625	A	30-10-1996	FR 2718961 A1	27-10-1995
			EP 0739625 A1	30-10-1996
			AT 202276 T	15-07-2001
			AU 1629295 A	16-11-1995
			BR 9501395 A	05-03-1996
			CA 2147550 A1	23-10-1995
			CA 2147553 A1	23-10-1995
			CN 1114681 A ,B	10-01-1996
			DE 69521414 D1	26-07-2001
			DE 69521414 T2	18-10-2001
			ES 2158056 T3	01-09-2001
			HU 71724 A2	29-01-1996
			JP 2912186 B2	28-06-1999
			JP 8059443 A	05-03-1996
			PL 308284 A1	30-10-1995
			AU 683347 B2	06-11-1997
			KR 188577 B1	01-06-1999
			RU 2127580 C1	20-03-1999
			US 5661118 A	26-08-1997
US 5661118	A	26-08-1997	FR 2718961 A1	27-10-1995
			AU 683347 B2	06-11-1997
			AU 1629295 A	16-11-1995
			BR 9501395 A	05-03-1996
			CA 2147550 A1	23-10-1995
			CA 2147553 A1	23-10-1995
			CN 1114681 A ,B	10-01-1996
			EP 0739625 A1	30-10-1996
			HU 71724 A2	29-01-1996
			JP 2912186 B2	28-06-1999
			JP 8059443 A	05-03-1996
			KR 188577 B1	01-06-1999
			PL 308284 A1	30-10-1995
			RU 2127580 C1	20-03-1999
EP 1166766	A	02-01-2002	EP 1166766 A1	02-01-2002
			US 6685953 B1	03-02-2004
			CN 1347312 T	01-05-2002
			WO 0061097 A1	19-10-2000
			US 2004115162 A1	17-06-2004

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82